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<https://doi.org/10.18297/etd/1951>

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UNIVERSITY OF LOUISVILLE

STUDIES IN THE DIPHENYL SERIES:
MONOHYDROXY DIPHENYLS

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

Department of Chemistry

By

ELIZABETH KENDRICK TRAWICK

1931

16 June '33 m.p.s.

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INTRODUCTION

INTRODUCTION

Due to the fact that diphenyl can now be produced in large quantities and at a low cost by the pyrolysis of benzene, its commercial possibilities have increased immensely. Commercially available, but little used compounds always arouse the interest of the research worker. It is his function to find an application for products of this type. In the diphenyl series we find just such a group. Diphenyl itself is now being used mainly as a heat transfer medium. Some of the derivatives, the chlorodiphenyls particularly, are used in the varnish and wax industries. The hydroxy diphenyls, if they react normally, might well serve as the starting point for syntheses involving the introduction of the diphenyl grouping. They also possess most of the desirable physical properties shown by other members of the series. The diphenyl radical is being substituted quite often for the phenyl radical in many methods for the preparation of dyes, drugs, and intermediates.

The hydroxy compounds, ortho and para, may be prepared by the following methods:

a. By warming one part of the potassium salt of diphenyl sulfonic acid with three parts of potassium hydroxide (1).

b. From amino diphenyl through the diazo reaction (2).

c. By warming an aqueous solution of benzene diazoniumchloride with phenol (3).

d. As a by-product from the hydrolysis under pressure of chlorobenzene (4). This last method furnishes the commercially available supply of ortho- and para-hydroxy diphenyl.

When the hydroxyl group is in the position ortho to the second ring the compound seems to be a simple substituted phenol. The sodium salt is easily prepared by dissolving the ortho phenyl phenol in a solution of sodium hydroxide and evaporating to dryness. The Kolbe reaction has been carried out on the sodium salt of ortho hydroxy diphenyl to give a very satisfactory yield (5).

The para-hydroxy diphenyl, on the other hand, is almost powdery in appearance and possesses no appreciable odor. If this compound were merely a substituted phenol there should be no difficulty in preparing the sodium salt, nor in running the Kolbe synthesis on it. In this respect, however, there is no evidence in the literature as to whether or not this reaction has been carried out on the para-hydroxy diphenyl.¹

1. In a private communication from Dr. Britton of the Dow Chemical Company, the information has been conveyed that they have carried out this reaction and received a yield of only 7%.

It is well known that the position of the substituents on a benzene ring directly affects their reactivity. This is shown in the case of the cresols(6) where the meta derivative was more reactive than the para, which in turn was more reactive than the ortho. There is a possibility that the presence of the phenyl group in the position para to the hydroxyl group will so affect the reactivity of the hydroxyl as to render it non-phenolic or very weakly so. The phenolic group is acidic in behavior while the alcoholic group is more nearly neutral in reaction. If para-hydroxy diphenyl is not a phenol, despite its attachment to a benzene ring, the hydroxyl group should be replaceable by a halogen when heated with halogen acids.

PRELIMINARY EXPERIMENTAL

1. Sulfonation of Diphenyl

In the preparation of hydroxy diphenyl the sulfonic acid method was used. (1) Since no definite temperature conditions were stated in the preparation of the acid, several preliminary runs were made to determine the optimum conditions for sulfonation of diphenyl. The product was isolated as the diphenyl monosulfonic acid.

In the first run 15.4 grams (0.1 mol) diphenyl and 46.2 grams (0.47 mol) sulfuric acid were used. The two substances were heated together on a boiling water bath, under a reflux condenser. After heating for forty hours the upper layer of liquid diphenyl disappeared and the mixture was removed from the flask to a beaker and diluted to 800 c.c. This was heated to boiling and an excess of copper oxide added, the mixture was then filtered while hot, and the filtrate allowed to stand over night. The copper salt of diphenyl monosulfonic acid was precipitated. This was treated with hydrochloric acid to form the diphenyl monosulfonic acid. A yield of 3.5 grams corresponding to 15% of the theoretical was procured.

A second run, containing the same amounts, but heated on a steam bath for twenty-five hours, gave the same yield.

In a third run the same amounts of the diphenyl and the acid were heated to 150° on an oil bath for seven hours. This experiment gave 4.7 grams corresponding to a yield of 20%.

A fourth run was made using 1 gram boric acid as a catalyst (7). The disappearance of the upper layer still required twenty-six hours of heating on a water bath but the yield was increased to 5.87 grams, 25%.

In a fifth run 46.3 grams of fuming sulphuric acid were used. After 15 hours of heating on a water bath the yield was only 1.17 grams or 5%.

A sixth run repeated the conditions of the third run, but gave only a 3.5 gram yield or 15%.

The seventh was the most satisfactory run. In this an automatic glass stirrer was attached through the condenser. The reaction mixture was heated on an oil bath at 150° for three hours. At the end of this time there was a 5 gram yield.

There seemed to be no appreciable increase in the amount of the disulfonic acid.

2. Reactions of Phenyl Phenols with Ferric Chloride.

Instead of giving the usual red coloration with a freshly prepared aqueous solution of Ferric Chloride, the alcoholic solution of both the ortho- and para-hydroxy diphenyl gave a dark green precipitate which disappeared leaving a green solution. This color gradually faded and finally remained a deep yellow.

3. Kolbe Synthesis with Phenol.

A trial run of the Kolbe reaction was made on phenol in order to check technique. The sodium salt was prepared, using $12\frac{1}{2}$ grams (0.3mol) sodium hydroxide and 30 grams (0.3mol) crystallized phenol. The salt was carefully dried, and heated in a retort while a current of dry carbon dioxide was passed over the solid (8). After heating for seven hours and raising the temperature to 200° the reaction was complete.

One half the phenol was converted to salicylic acid and the other half sublimed according to the following reactions:

The theoretical yield, computed on a basis of one-half the phenol used, was 20.5 grams. The yield was 5 grams, 25%.

4. Kolbe Synthesis with Ortho-Hydroxy Diphenyl.

The same experiment was repeated using ortho-hydroxy diphenyl (9). 17 grams (0.1mol) of the ortho phenyl phenol were heated with 4 grams (0.1mol) sodium hydroxide to form the sodium phenyl phenate(5). The salt was carefully dried as in the case of the phenol and then similarly heated in a retort with a current of dry carbon dioxide passing over it. The phenyl salicylic acid (sodium salt) was purified by dissolving it in sodium carbonate, filtering off the impurities, extracting the solution with ether, and adding hydrochloric acid to precipitate the ortho-phenyl salicylic acid.

The acid was then recrystallized from hot ethyl alcohol. There was a 3 gram yield corresponding to 33% of the theoretical.

FINAL EXPERIMENTAL

1. Kolbe Synthesis on Para-Hydroxy Diphenyl

4 grams (0.10 mol) sodium hydroxide were dissolved in 20 c.c. water. Then 17 grams (0.1 mol) para-hydroxy diphenyl were added. The para-hydroxy diphenyl would not dissolve as an ordinary substituted phenol should, so 20 c.c. more of the sodium hydroxide solution were added, but it still would not dissolve. When heat was applied the diphenyl compound melted but still would not combine, for upon cooling there settled out a crystalline substance melting at 163°. After refluxing for thirty-five hours there was some change in the crystalline substance. At a temperature of 200° there was decomposition, but no melting. When fused on a crucible cover there remained a metallic residue which gave a basic reaction with phenolphthalein, indicating presence of some sodium phenyl phenate. However, upon attempted recrystallization from hot water the substance hydrolyzed to give sodium hydroxide and para-hydroxy diphenyl, melting at 163°. A commercial sample behaved in the same manner.

An alcoholic solution of sodium hydroxide was heated with para-hydroxy diphenyl but after thirty-two hours of refluxing there was no evident change in the para-hydroxy diphenyl.

1
 10 grams (0.5mol) dry sodium para-phenyl phenate
 were placed in a 500 c.c. retort which was immersed
 as far as possible in an oil bath. For one half hour
 a current of dry hydrogen was passed into the retort
 which was heated to a temperature of 140°. This was done
 to insure absolute dryness of the sodium salt. The
 retort was allowed to cool to 110°, and a stream of
 dry carbon dioxide was passed in for one hour. Then
 the temperature was raised 20 degrees an hour for four
 hours, reaching 190°. For one hour the temperature was
 held at 200°. Carbon dioxide was passed in during the
 whole six hours. At almost 110° a sublimation of
 hydroxy diphenyl took place. About half the original
 amount was deposited on the sides of the retort above
 the oil bath. This reaction takes place at about the same
 temperature as a similar sublimation of phenol and
 ortho hydroxy diphenyl. Upon completion of the re-
 action the product was removed and purification
 attempted. However, when the hydrochloric acid was added
 to the precipitate, the para phenyl salicylic acid
 there was an evolution of gas. This was shown to be
 carbon dioxide by passing it through lime water which
 resulted in a precipitation of calcium carbonate.
 The solid that was left after all the gas passed off
 was para-hydroxy diphenyl, melting at 163°. Evidently
 the reaction had gone, not to completion, but through
 the first stage only, thus:

$$C_6H_5C_6H_4ONa + CO_2 \rightarrow C_6H_5C_6H_4O \cdot COONa$$

 1. Commercial product furnished by the Dow Chemical
 Company.

When hydrochloric acid is added to the compound carbon dioxide is easily driven off and the sodium replaced by a hydrogen to give para-hydroxy diphenyl, sodium chloride, and carbon dioxide.

2. Para Hydroxy Diphenyl with Hydrochloric Acid.

In a 500 c.c. round bottom flask 60-70 cubic centimeters of water were placed, 7.6 grams (0.13mol) sodium chloride added and the solution shaken thoroughly to avoid lumping. Then 17 grams (0.1mol) para-hydroxy diphenyl were added. A reflux condenser was attached and 25.5 grams (0.26mol) concentrated sulfuric acid were added in 10 c.c. portions through the condenser while the flask was being shaken. After all the acid was added a glass tube bent in the shape of a U was connected to the condenser at one end and to a funnel inverted over 300 c.c. of water in a beaker at the other end. This was to absorb any fumes of hydrochloric acid gas that might come over. The flask was refluxed on a wire gauze for two hours, then, since there was no change in the hydroxy diphenyl, more acid was added making a total of 94 mols. Heat was again applied and the mixture refluxed for seven hours. Some of the para-hydroxydiphenyl sublimed or was carried up by the hydrochloric acid gas. There were two layers in the flask. The top one was solid unchanged hydroxy diphenyl.

The lower layer which was liquid contains a white substance in suspension. Some of this crystalline compound was dried and found to melt at 160° . A mixed melting point with a known specimen of para-chloro diphenyl showed the two to be different. This substance was evidently unchanged hydroxy diphenyl. No substitution of a chlorine atom for a hydroxyl group had taken place.

3. Para Hydroxy Diphenyl with Hydrobromic Acid.

In the same type of set up were placed 30 c.c. water, 13.3 grams (0.13mol) sodium bromide, 17 grams (0.1mol) para-hydroxy diphenyl and 93 grams (0.94mol) concentrated sulfuric acid. After refluxing for one and one quarter hours the upper layer melted and became a dark brown oily liquid. Upon cooling after two hours of heating this top layer became a white solid cake, melting from 120° to 145° . At this point 50 c.c. of 40% solution of hydrobromic acid were added and the contents of the flask refluxed for two more hours. At the end of that time the melting point of the top layer (solid when cold) was 120° - 125° . The crystals in the lower liquid melted 70° - 90° . After heating for three hours more, a total of seven hours, the top layer was visibly diminished and melted 75° - 100° . The crystals from the lower liquid melted at 75° - 85° . The mixture was heated for a total of 17 hours. At each cooling the upper layer became a solid, each time a little darker in

color until finally it was a brownish purple. Many means of purification were attempted, including recrystallization from hot water, hot ethyl, methyl and butyl alcohols, acetic acid, and finally steam distillation. The melting point remained between 75°-80°, never a sharp melting point, however. A mixed melting point with para bromo diphenyl¹ was 50°, indicating that the prepared product was not para bromo diphenyl. Para bromo diphenyl has a melting point of 89°-90° (9). The commercial sample used for mixed melting point, however, had a melting point of 75°.

A second run was started using 200 c.c. of 40% solution of hydrobromic acid and 17 grams (0.1mol) para hydroxy diphenyl. After fifteen hours of refluxing, there was no apparent change in the compound.

A third run was made in a pressure flask. A saturated solution of hydrobromic acid was prepared and two grams of para hydroxy diphenyl added. The flask was immersed in a water bath and heated to 60° for five hours. Then the solution was resaturated and the flask heated in boiling water for six hours. There was no change in the compound.

1. Commercial product furnished by Dr. Gilman of Iowa State College, Ames, Iowa.

CONCLUSIONS

CONCLUSIONS.

In the sulfonation of diphenyl the maximum yield was obtained when the reaction mixture was heated and stirred for three hours at 150°. The use of boric acid as a catalyst did not facilitate the speed of the reaction at all, nor did the use of fuming sulfuric acid.

Ortho phenyl phenol had the appearance and general physical characteristics of a substituted phenol. It responded to all chemical reactions for a phenol, with the exception of the color formation with ferric chloride. The appearance of a green coloration instead of the usual red might have been due to the presence of the diphenyl radical. The Kolbe reaction went to the extent of 25%, indicating that ortho hydroxy diphenyl was a phenol and could be expected to react as a phenol does.

The para hydroxy diphenyl on the other hand, did not show such marked phenolic behavior. Its physical characteristics were not phenolic, and the Kolbe syntheses, which is generally accepted as a reaction for that type of compound, did not go to completion. If, however, the hydroxyl group were alcoholic, the bromine substitution should have taken place, but results from that experiment indicated that the bromine had not replaced the hydroxyl. So the evidence was not strong enough to state that this was an alcoholic hydroxyl group.

The other possibility was that the bromine had replaced a hydrogen to enter the ring. Since the sulfuric could oxidize the hydrobromic acid thus:

giving free bromine, this hydrogen replacement could easily have occurred. There was no evidence in the literature that such a compound had ever been prepared so it was necessary to make a quantitative analysis of the unknown substance. Up to the present time that analysis has not been completed, so it is not fully determined whether the bromine has entered the ring, which ring it has entered, or in what position.

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AUTOBIOGRAPHY

Elizabeth Kendrick Trawick was born August 11, 1908 in Louisville, Kentucky. She received her early schooling in the Louisville Public Schools, and in the Louisville Girl's High School. In September 1926 she entered the University of Louisville. Chemistry was her major subject, and she was graduated from that institution in June, 1930, with the degree of Bachelor of Science. At that time she was awarded the fellowship given by the Paint, Oil and Varnish Club of Louisville to be used for graduate work in Chemistry. She applied for the Degree of Master of Science in 1931.